THE IPR ISOMERS OF C_{80}: SAM1 COMPUTATIONS

MEI-LING SUN, ZDENĚK SLANINA*, SHYI-LONG LEE
Department of Chemistry, National Chung-Cheng University
Ming-Hsiung, Chia-Yi 62107, Taiwan

FILIP UHLÍK
Faculty of Science, Charles University, CZ-12000 Prague 2, Czech Republic

LUDWIK ADAMOWICZ
Department of Chemistry, University of Arizona, Tucson, AZ 85721, USA

ABSTRACT

The complete set of seven isolated-pentagon-rule isomers of C_{80} is computed by
the SAM1 quantum-chemical method. The ground-state structure is a D_{5d} isomer
but at elevated temperatures a D_{2} structure is the most populated one. The results
essentially agree with the AM1 computations.

1. Introduction

In contrast to other higher fullerenes, esp. C_{78}, C_{82}, C_{84}, the in-between
system, C_{80}, has received a limited attention\(^1,2\) apparently because the particular
fullerene set has not been isolated yet\(^3,4\). Recently we computed the C_{80} IPR set
by the AM1 method\(^5\) and the present paper is a continuation of the research, using
the newest member of the semiempirical family, the SAM1 method\(^6\).

Fullerene systems cannot be understood without considering temperature ef-
fects. Although inter-isomeric separation energies are important, they are not the
only parameters responsible for the relative stabilities at elevated temperatures.
The temperatures in fullerene syntheses are high and thus, entropy factors can play
an important role. There are seven topologically different C_{80} structures\(^7\) which
obey the IPR rule (they are coded A-G which correspond to the letters used in
Ref. 2, see Figure 1).

2. Calculations

The geometry optimizations were performed with the implementation of the
SAM1 semiempirical quantum-chemical method in the AMPAC program package\(^8\).
The optimizations were carried out without any symmetry constraints in Cartesian
coordinates and with the analytically constructed energy gradient, starting from
the AM1 optimized geometries\(^9\) (preliminary computations were also done with the
SPARTAN and GAUSSIAN 92 packages\(^9,10\)). In the SAM1 optimized geometries,
the harmonic vibrational analysis was performed by a numerical differentiation of

* On a leave of absence from the Academy of Sciences of the Czech Republic, Prague.
To whom correspondence should be addressed at the NCCU.
Figure 1. The IPR structures of $C_{80}$. 
Table 1. The SAM1 symmetries, rotational constants $A$, $B$, $C$, and energetics$^a$ of the IPR structures of $C_{80}$

<table>
<thead>
<tr>
<th>Species</th>
<th>$A$</th>
<th>$B$</th>
<th>$C$</th>
<th>$\Delta H_f^{o,298,rel}$</th>
<th>$\Delta E_{rel}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
<td>(kJ/mol)</td>
<td>(kJ/mol)</td>
</tr>
<tr>
<td>A $D_2$</td>
<td>0.00138</td>
<td>0.00145</td>
<td>0.00173</td>
<td>16</td>
<td>17</td>
</tr>
<tr>
<td>B $D_2$</td>
<td>0.00151</td>
<td>0.00151</td>
<td>0.00152</td>
<td>290</td>
<td>314</td>
</tr>
<tr>
<td>C $D_{5d}$</td>
<td>0.00138</td>
<td>0.00138</td>
<td>0.00182</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>D $C_{2v}$</td>
<td>0.00150</td>
<td>0.00151</td>
<td>0.00152</td>
<td>138</td>
<td>154</td>
</tr>
<tr>
<td>E $C_{2v}$</td>
<td>0.00141</td>
<td>0.00151</td>
<td>0.00162</td>
<td>69</td>
<td>75</td>
</tr>
<tr>
<td>F $C_2$</td>
<td>0.00135</td>
<td>0.00159</td>
<td>0.00161</td>
<td>126</td>
<td>138</td>
</tr>
<tr>
<td>G $C_s$</td>
<td>0.00146</td>
<td>0.00151</td>
<td>0.00158</td>
<td>105</td>
<td>115</td>
</tr>
</tbody>
</table>

$^a$ Relative heats of formation at room temperature ($\Delta H_f^{o,298,rel}$) or relative potential energies ($\Delta E_{rel}$).

Table 2. The SAM1 gas-phase equilibrium relative populations $w_i$ of the IPR structures of $C_{80}$

<table>
<thead>
<tr>
<th>$w_i$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (K)</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>500</td>
</tr>
<tr>
<td>1000</td>
</tr>
<tr>
<td>1178$^a$</td>
</tr>
<tr>
<td>1500</td>
</tr>
<tr>
<td>2000</td>
</tr>
<tr>
<td>2300$^a$</td>
</tr>
<tr>
<td>2500</td>
</tr>
<tr>
<td>3000</td>
</tr>
<tr>
<td>4000</td>
</tr>
<tr>
<td>5000</td>
</tr>
</tbody>
</table>

$^a$ Two-structure equimolarity point.
the analytical energy gradient. Relative concentrations $w_i$ were computed using the rigid-rotor and harmonic-oscillator partition functions\textsuperscript{11}. Chirality contribution was considered for the $C_n$ and $D_n$ symmetries.

3. Results and Discussion

The $B$ species has a topological symmetry $I_h$, but it undergoes a Jahn-Teller distortion towards lower energy and lower symmetry, $D_2$ - Table 1. The determination of the symmetry is not an easy task but the SAM1 results are actually more consistent comparing to the AM1 computations\textsuperscript{5}. The SAM1 computations predict (Table 1) the $C$ isomer ($D_{5d}$ symmetry) as the system ground state, being followed by the $A$ species of a $D_2$ symmetry. The vibrational calculations confirmed that all the seven localized stationary points are local energy minima. Table 2 reports the temperature evolution of the relative concentrations, $w_i$, for the seven-membered mixture under the thermodynamic-equilibrium conditions. At very low temperatures the ground-state structure, $C$, has to be prevailing. At a temperature of 1178 K the $A$ species reaches equimolarity with the $C$ species, and also other species become gradually significant. At about 2300 K the $F$ species reaches equimolarity with the $C$ isomer, too. The isomeric interplay can also be visualized in terms of the isomerism contribution to heat capacity, $\delta C_p,C$, which has a sharp maximum of 76.1 J.K$^{-1}$.mol$^{-1}$ at 2160 K.

In overall, the SAM1 computations predict that under the supposed fullerene-synthesis conditions the species $A$ and $C$ should primarily be produced, and possibly other isomers in less significant concentrations. The SAM1 results essentially agree with the AM1 ones\textsuperscript{5} though there are some differences for less populated species.

4. Acknowledgments

Acknowledgements are made to the National Science Council, Taiwan, Republic of China and to the NCHC, Hsinchu for computer time on the Convex C3840.

5. References
8. AMPAC 5.0 (Semiche, Shavnee, KS, 1995).